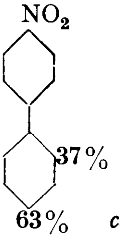
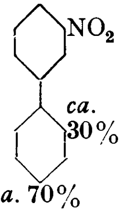
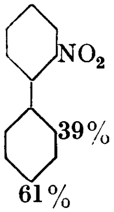
237. *Inductive Effects in the Diphenyl Series.*

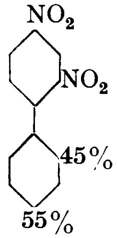
By C. G. Le Fèvre and R. J. W. Le Fèvre.

Le Fèvre and Turner (J., 1928, 247) concluded that the two nuclei of diphenyl derivatives were independently conjugated from the fact that, whatever the nature or position of the radical X, the phenyl group in any compound $C_6H_5{\cdot}C_6H_4X$ was always substituted by electrophilic reagents at the *o*- or *p*-carbon atoms. Later, Gull and Turner (J., 1929, 491) quantitatively exemplified this generalisation by a study of the mononitrations of the substances shown in the accompanying formulæ. The figures indicate the proportions in which the entrant nitro-groups had effected substitution. In no case did there seem to be more than 1% of a third substance; thus it appeared that the extensive electronic rearrangements necessary for orientation and other similar activation effects in aromatic molecules were not transmitted across the 1 : 1′-link, which therefore did not seem to be part of a conjugated system.







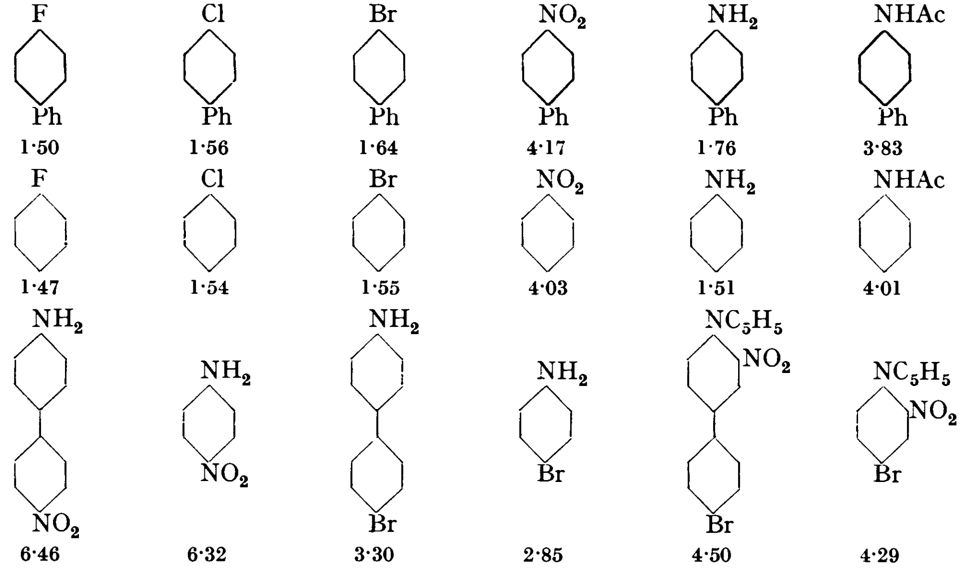


With a clearer recognition that relative orientative action and velocities of substitution at the various positions are fundamentally connected, the above conclusion—as stated—seems likely to be an exaggeration. Many experimental facts have demonstrated a certain mutual dependence of the nuclei; *e.g.*, conditions which suffice to dinitrate benzene or toluene must be employed to mononitrate 4-nitrodiphenyl—the unsubstituted phenyl group of which is clearly deactivated by the nitro-group situated at the extreme end of the other nucleus.

Superficially, therefore, it would appear that the diphenyl structure presents the features that general inductive influences are transmitted right through the molecule, but that extensive tautomeric displacements are so reduced at the bridge bond that they can exert no effects observable by substitution reactions in the attached ring. Their development in this nucleus might, however, be inferable from a study of the mesomerism (Ingold, *Chem. Reviews*, 1934, **15**, No. 2) of various diphenyl compounds, since the mesomeric and tautomeric effects operate by the same mechanism, and the presence of one can be taken as evidence of the possibility of the other.

Information on these points, from dipole-moment measurements on some diphenyl compounds, together with a consideration of the possible inductive effects, is the subject of the present paper.

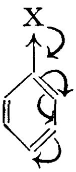
Accordingly, we record a number of comparisons of the dipole moments of 1 : 4-XY-substituted benzenes with the analogous 4 : 4′-XY-diphenyls. The results (in Debye units) are shown below the appropriate formulæ :



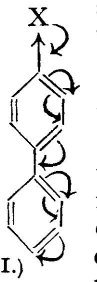
These moments have been obtained by reckoning ${}_{0}P = {}_{T}P - [R_L]_D$, thus the full correction for ${}_{A}P$ has probably not been made, and the data for the diphenyl derivatives may be slightly more erroneously high than those for the corresponding benzene compounds. The order of such excess is, however, probably quite low. This we infer from our previous demonstration (this vol., p. 487) that with the same apparatus and technique the total polarisations of diphenyl and its *pp*′-dichloro-derivative (both having $\mu = 0$) exceed the $[R_L]_D$ values only very slightly. All refer to benzene solutions.

Discussion.—As a basis it is assumed that the diphenyl molecule is collinear, the zero moments of the 4 : 4′-dihalogenodiphenyls (Williams, *J. Amer. Chem. Soc.*, 1928, **50**, 2350) and the *X*-ray data (Clark and Pickett, *J. Amer. Chem. Soc.*, 1931, **53**, 167, 3820; Dhar, *Indian J. Physics*, 1932, **7**, 43) adequately justifying such an assumption.

The mesomeric effect in an aromatic molecule is defined as a permanent electronic rearrangement occurring by the mechanism of the tautomeric effect (Ingold, J., 1933, 1120; and *loc. cit.*). Thus the mesomeric state of a monohalogenobenzene and a similarly substituted diphenyl can be represented by attaching to one of the unperturbed forms (I) or (II) the curved arrows commonly used to indicate electromeric changes (Ingold, *locc. cit.*). In the series of compounds now under discussion, it is therefore evident that (X being halogen) the *observed* moment will consist of the natural moment of the C—X link *plus* all the induced moments arising from the interaction of the C—X moment with the polarisable atoms constituting the rest of the molecule *minus* the small *but permanent* moments caused by the mesomeric effect. The last-named polarisation is difficult to estimate, but its existence is held to explain why the halogenobenzenes have smaller moments than the corresponding *tert.*-butyl halides in which no such reversed moments are operative (cf. *Ann. Reports*, 1931, **28**, 393). If the process illustrated in (II) were to occur to any extent, therefore, the 4-halogenodiphenyls should show greater *reversed* (+ *M*, cf. Ingold, *loc. cit.*) polarities than the related benzene compounds, and one might expect the *observable* dipole moments to be smaller than those of the benzene derivatives by roughly the amount of these *M* changes.



(I.)

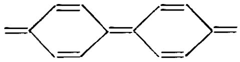


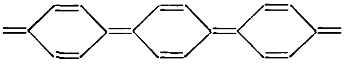
(II.)

However, as shown above, the experimental data do not bear out this forecast, and it would therefore appear either that the moments induced in the unsubstituted phenyl nuclei by the distant C—X moments outweigh the reversed (mesomeric) moments, or the mesomeric effect is not transmitted across the 1 : 1′-bond.

That the latter suggestion is most probably incorrect follows from the work of Dhar (*loc. cit.*) on diphenyl and of Pickett (*Nature*, 1933, **131**, 513; *Proc. Roy. Soc.*, 1933, **142**, *A*, 333) on *p*-diphenylbenzene (terphenyl). In both cases *X*-ray examination shows the molecules to consist of flat regular hexagons of carbon atoms lying in one plane, with distances between consecutive atoms in each ring from centre to centre of 1·42 A. The C—C bond length between the nuclei is given as only slightly longer, *viz.*, 1·48 A. This is significantly shorter than the normal single bond length (1·54 A.) and constitutes direct evidence that the hydrocarbons at least are degenerate, with structures between the unperturbed forms represented by the singly linked Kekulé individuals, on the one hand, and the forms (III) and (IV), on the other.*

(III.)





(IV.)

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* We take this opportunity to point out an implication of this result on the question of dissymmetry in the diphenyl series. Le Fèvre and Turner (*Chem. and Ind.*, 1926, **45**, 831) considered that by virtue of conjugation, etc., the two nuclei of any diphenyl compound tend to be coplanar, but that certain groups in three of the 2 : 2′ : 6 : 6′-positions necessitate by their electrical, mass, or volume effects the adoption of the non-coplanar configuration which is made manifest by optical activity. Mills (*ibid.*, pp. 883, 905) and Bell and Kenyon (*ibid.*, p. 864; J., 1926, 3045), on the other hand, preferred the view that groups were effective because by their " obstacle " action *free rotation* of the two nuclei was inhibited. In each of the explanations, of course, the ultimate cause of the enantiomorphism was the non-coplanarity of the nuclei.

Since 1926, the following pertinent facts have become available : (1) that in the crystal the phenyl nuclei of diphenyl are coplanar (Clark and Pickett; Dhar; Pickett, *locc. cit.*), and (2) that the 1 : 1′-bond

Mesomeric effects therefore can occur in diphenyl itself; it seems unlikely that they would be absent from derivatives of this hydrocarbon. Hence it becomes necessary to investigate the other possible explanation for our results, and to attempt to estimate the magnitudes of the subsidiary moments which could be induced in the molecules by the principal moments in each case.

Calculation of the Induction by the Chief Permanent Moments.—These calculations have been carried out for the four substances with axially symmetrical groups, the internuclear distances and atomic radii shown in the scale drawings (Figs. 1, 2, and 3) being used. For 4-nitro- and the two 4-halogeno-diphenyls (Figs. 1 and 2 respectively) the moments induced at the centre of gravity of the phenyl radical (μ_x) should equal $2\mu\alpha(\varepsilon + 2)/3\varepsilon r^3$ and operate in the direction of the chief permanent moment. The distance r has been taken from the centre of the nitrogen atom in Fig. 1, and from the points of contact between the halogen atoms and the carbon atom in Fig. 2, to the mass centre of the polarisable phenyl groups. The polarisability, α, adopted for the latter is that for the plane of the benzene ring (cf. Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 121), *viz.*, $1{\cdot}23 \times 10^{-23}$ e.s.u.; the dielectric constant of the medium through which the inductive force acts is assumed to be roughly that of benzene, *viz.*, 2·3. The sum of the induced and the permanent moment is, in each case, to be compared with the observed figure (see

FIG. 1.

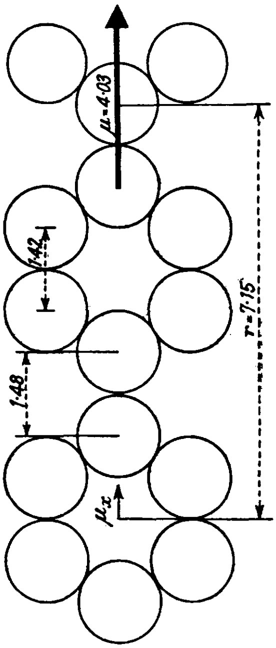


FIG. 2.

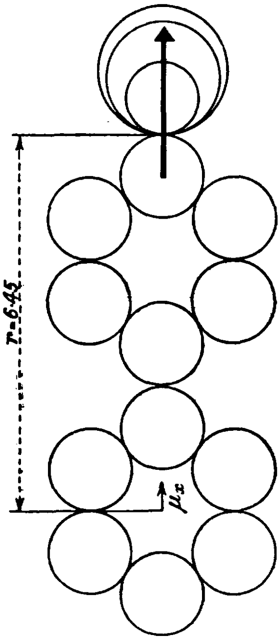
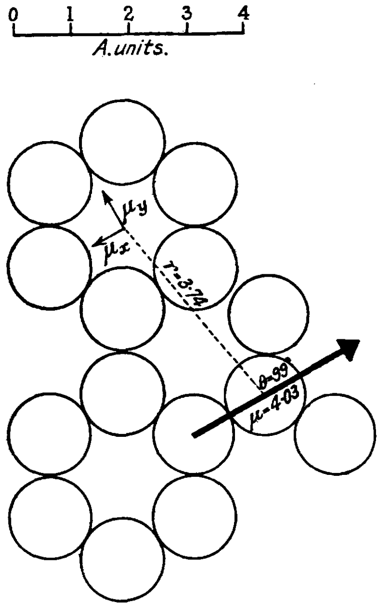


FIG. 3.



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is intermediate between a single and double link (*idem, ibid.*). Therefore it, like all the other bonds of a conjugated system, is degenerate. The observed shortening of the 1 : 1-bond is the modern external indication to be expected for the " conjugation," etc., considered by Le Fèvre and Turner (*loc. cit.*) to be the mechanism whereby the nuclei are held as far as possible coplanar. It could now be expressed better by saying that, from experimental evidence, the 1 : 1′-link should possess to some degree the torsional rigidity of a double bond. Further, during the last 10 years no evidence seems to have been advanced that free rotation of the nuclei occurs in the *absence* of effective obstacle groups.

Thus the approximation of the real structure of diphenyl to (III) and of the 1 : 1′-link to a double bond, besides rationalising a stabilised planar configuration of the nuclei, affords an explanation of the observation by Harries and Weiss (*Annalen*, 1905, **343**, 374) that diphenyl will form only a tetraozonide, and not the hexaozonide to be expected from a molecule containing six olefinic linkings.

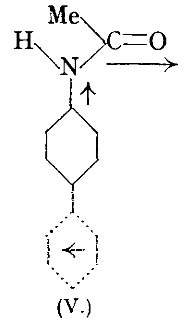
first four lines in following table, in which r, the distance from the mass centre to the seat of the dipole, is given in A.) :

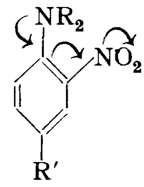
Diphenyl compound.	Parent halogenobenzene and its moment.	r.	$\mu_{calc.}$.	$\mu_{obs.}$.
4-Fluoro	PhF 1·47	6·45	1·55	1·50
4-Chloro-	PhCl 1·54	6·45	1·63	1·56
4-Bromo-	PhBr 1·55	6·45	1·64	1·64
4-Nitro-	$PhNO_2$ 4·03	7·15	4·20	4·17
2-Nitro-	,, ,,	3·74	3·44	3·8
4-Amino-	$PhNH_2$ 1·51	6·45	1·60	1·76

The observed moments of fluoro- and chloro-diphenyls lie closer to those of the corresponding benzene derivatives than to the calculated values; with bromodiphenyl there is (fortuitously good) agreement between the observed and calculated figures, whilst for 4-nitrodiphenyl the calculated is slightly higher than the found moment, both of which are considerably greater than that of nitrobenzene.

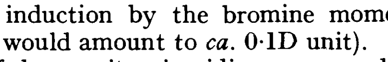
Mesomerism.—Thus it would appear that in the fluoro- and chloro-compounds the mesomeric (as in formula II) more nearly outweighs the inductive polarisation than it does in the bromo-derivative; *i.e.*, the mesomeric effects are for these halogens in the order F and Cl > Br. This is in conformity with a recent statement by Ingold (*Chem. and Ind.*, 1935, **13**, 1079) that mesomeric and electromeric changes need not necessarily run parallel in a given series, such as the halogens; however, for the nitro-group (for which by older reasoning, *e.g.*, slight occurrence of *op*-substitution reactions with nitrobenzene, indicating little development of $+E$ changes, a large $+M$ would not be expected) we find the induced polarity much more nearly sufficient to account for the observed increase in moment (0·14D). Owing to the configurational uncertainties of the $-NH_2$, the $-NHAc$, and the $-NC_5H_5$ groupings, calculations of the above types for the compounds containing these radicals will not be discussed; the data for aniline are included in the table.

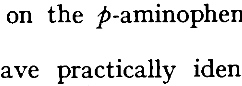
Qualitatively the results for acetanilide and 4-acetamidodiphenyl are what one would expect if the resultant moment of the first compound were to be regarded crudely as compounded of the C—O and the C—N moment (see V). In the diphenyl derivative the former component will be diminished by the reverse induced moment in the free nucleus. The resultant will therefore be smaller.


(V.)


(VI.)

The two disubstituted diphenyls show considerable mesomerism, the moments of *p*-nitroaniline and 4-nitro-4′-aminodiphenyl being very close, and both larger than the sum $\mu_{NH_2Ph} + \mu_{PhNO_2}$. The small excess of the moment of the diphenyl compound over the benzene derivative can be largely attributed to induction. The cases of bromoaniline and bromoaminodiphenyl are different in that, whilst the last comparison involved two groups in positions where their M effects could be complementary, these are cases where two like radicals are in competition. Presumably the process $\overset{\curvearrowright}{NH_2}\cdot C_6H_5$ occurs more readily than $\overset{\curvearrowright}{Br}\cdot C_6H_5$: the increase of 0·45D unit can therefore be explained by a differential mesomerisation





plus a certain induction by the bromine moment on the *p*-aminophenyl nucleus (by calculation this would amount to *ca.* 0·1D unit).

The pair of bromonitropiperidino-compounds have practically identical moments, although they contain the essential structures of the previous substances respectively. No mesomeric changes throughout the diphenyl molecule can therefore be operative; it is probable that the mesomerism involved in (VI) causes greater stabilisation than would be effected by mesomerisation of the type (II), the contribution of which to the real structure can therefore be ignored.

2-*Nitrodiphenyl*.—A calculation of the moment of this compound has been attempted with the following premises (cf. Fig. 3): $r = 3{\cdot}74$ A., $\theta = 99°$, α (for plane of benzene ring) $= 1{\cdot}23 \times 10^{-23}$, α (for thickness of benzene ring) $= 0{\cdot}635 \times 10^{-23}$, $\mu = 4{\cdot}03 \times 10^{-18}$ e.s.u.

For the induced moments in the coplanar position we have

$$\mu_x = (\alpha\mu/r^3)(3\cos^2\theta - 1)(\varepsilon + 2)/3\varepsilon = 1{\cdot}14 \times 10^{-18}$$

and

$$\mu_y = (3\alpha\mu/r^3)(\sin\theta \, . \cos\theta)(\varepsilon + 2)/3\varepsilon = 0{\cdot}27 \times 10^{-18}$$

and similarly for the induced moments when the nuclei are in planes intersecting at right angles:

$$\mu_x = 0{\cdot}59 \text{ and } \mu_y = 0{\cdot}14 \times 10^{-18} \text{ e.s.u.}$$

Therefore, if free rotation were possible, the mean μ_x and μ_y would be $\sqrt{2} \times 0{\cdot}55 + 0{\cdot}59 = 1{\cdot}37$D and $\sqrt{2} \times 0{\cdot}13 + 0{\cdot}14 = 0{\cdot}32$D respectively, and the resultant molecular moment of 2-nitrodiphenyl would become $(4{\cdot}03 - 1{\cdot}37)$ resolved with 0·32 at 90°, *i.e.*, $2{\cdot}7 \times 10^{-18}$ e.s.u. This is so much lower than the observed figure (3·8) that the inference is inevitable that the molecule is in the non-coplanar configuration to the maximum extent possible. On the basis of data given above, the moment of such a form is calculated as a minimum estimate (because r is probably too small) as 3·44D.

Comparable previous determinations of the moments of some of the substances discussed in this paper are collected in the following table.

Previous measurements in benzene solution.

Substance.	Moment.	Ref.	Substance.	Moment.	Ref.
4-Chlorodiphenyl	1·30—1·53	F	Bromobenzene	1·49—1·70	F
	1·63	N	Nitrobenzene	3·82—4·08	F
4-Nitrodiphenyl	4·28	N	Aniline	1·51—1·6	F
4-Aminodiphenyl	1·73	N	*p*-Nitroaniline	5·6 —7·1	F
Fluorobenzene	1·39—1·45	F	*p*-Bromoaniline	2·87—2·99	F
Chlorobenzene	1·5 —1·64	F			

F = *Trans. Faraday Soc.*, 1934, Appendix; N = Naeshagen, *Z. physikal. Chem.*, 1934, *B*, **25**, 158.

The following comments can be made on the above data. Their differences represent disagreements of measurement and not the use of different conventions in the calculations: they are practically all by the optical method with no correction for the atomic polarisation. The result of Estermann (*Z. physikal. Chem.*, 1928, *B*, **1**, 134) for aniline is based on only one solution; Hassel and Uhl (*ibid.*, 1930, *B*, **8**, 187) report a slight increase of polarisation with dilution, and Tiganik's measurements (*ibid.*, 1931, *B*, **14**, 135) for the same substance show practically no dependence on concentration. Our results confirm this behaviour. The divergent results for *p*-nitroaniline may be due to its sparing solubility at the ordinary temperature; therefore Tiganik's measurement, carried out at 70°, at which more concentrated solutions could be prepared, seems likely to be more correct than others. His value, 6·4D, compares favourably with ours. Bergmann and Tschudnovsky (*ibid.*, 1932, *B*, **17**, 100) report for *p*-bromoaniline the following P_{A+O} figures: 161·1, 164·2, 160·9, 159·5. These are in order of diminishing concentration and are extrapolated to 171·0 c.c. for infinite dilution. From our measurements we obtain 166 c.c. and a slightly lower moment. An increase of polarisation with dilution is noticed.

EXPERIMENTAL.

In the following tables, f_1 represents the molar fraction of the solute in each solution, d the density of the solution, ε the dielectric constant of the solution at *ca.* 1200 kc., and P_1 the apparent polarisation of the solute for the stated concentration f_1 at the temperature of measurement (25°). The solvent used was benzene throughout ($\varepsilon_{25°}$ 2·2725; $d_{4°}^{25°}$ 0·87380). The substances examined were pure specimens having the m. p.'s or b. p.'s recorded in the literature. For a number of them we are indebted to Dr. E. E. Turner.

4-Fluorodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
3490·0	2·2851	0·87532	98·3
4461·3	2·2880	0·87571	96·5
6999·9	2·2965	0·87677	95·9
9811·7	2·3058	0·87795	95·4

4-Chlorodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
3610·1	2·2872	0·87587	106·3
5021·1	2·2926	0·87670	105·6
7130·4	2·3006	0·87786	104·6
8612·11	2·3065	0·87880	104·3

4-Bromodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
925·5	2·2770	0·87485	116·2
2963·9	2·2857	0·87689	112·9
5000·1	2·2942	0·87890	111·9
5286·9	2·2955	0·87918	112·1

2-Nitrodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
1696·1	2·3075	0·87491	348·6
2871·6	2·3313	0·87565	345·2
3250·1	2·3385	0·87589	342·4
3697·3	2·3475	0·87617	341·6

4-Nitrodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
2057·4	2·3243	0·87516	413·2
2499·9	2·3356	0·87551	412·6
2881·0	2·3451	0·87578	411·2
4292·3	2·3780	0·87671	403·5

4-Aminodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
1668·9	2·2809	0·87457	117·3
2539·6	2·2858	0·87496	120·0
6792·5	2·3071	0·87677	118·7

4-Acetamidodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
101·81	2·2746	0·87384	362·5
138·26	2·2756	0·87386	387·7
230·29	2·2774	0·87386	375·6
290·25	2·2780	0·87389	340·4

4-Nitro-4′-aminodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
54·5	2·2757	0·87381	934
118·36	2·2799	0·87385	976
134·15	2·2801	0·87386	889
239·96	2·2864	0·87395	901

4-Bromo-4′-aminodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
852·26	2·2870	0·87487	295·3
1330·7	2·2938	0·87541	274·1
2114·5	2·3064	0·87632	282·1

4-Bromo-3′-nitro-4′-piperidinodiphenyl.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
278·00	2·2803	0·87425	484·9
290·10	2·2806	0·87429	480·5
304·99	2·2810	0·87432	479·7
318·64	2·2814	0·87436	478·9

Fluorobenzene.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
13834·0	2·3135	0·87592	71·2
26544·8	2·3496	0·87799	69·8
45941·0	2·4042	0·880931	68·9

Chlorobenzene.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
3804·8	2·2852	0·87479	79·3
4301·1	2·2880	0·87494	83·0
5777·8	2·2925	0·87534	80·8

Bromobenzene.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
25475·0	2·3628	0·89195	82·9
26044·3	2·3653	0·89271	82·7
34010·0	2·3902	0·89823	81·2
49686·3	2·4487	0·90950	81·9

Nitrobenzene.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
16110	2·6390	0·88035	337·5
20530	2·7411	0·88153	333·1
23887	2·8067	0·88298	322·8

Aniline.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
20716	2·3448	0·87709	77·2
26836	2·3658	0·87807	76·8
36815	2·4036	0·87964	77·5

Acetanilide.

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
1415·8	2·3050	0·87432	369·2
3506·4	2·3531	0·87501	366·8
4735·4	2·3808	0·87538	363·6

p-*Nitroaniline.*

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
2216·5	2·3980	0·87507	837
2500·0	2·4143	0·87523	835
3344·0	2·4627	0·87571	829
3471·96	2·4629	0·87580	800

p-*Bromoaniline.*

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
5501·1	2·3390	0·87925	203·2
15021	2·4551	0·88872	199·5
23513	2·5601	0·89701	196·9

*4′-Bromo-2′-nitro-*1*-phenylpiperidine.*

$10^6 f_1$.	ϵ_{25°.	$d^{25^\circ}_{4^\circ}$.	P_1.
685·98	2·2906	0·8741	442·4
1000·1	2·2991	0·87514	444·6
1499·8	2·3121	0·87579	441·2
2006·9	2·3252	0·87646	438·1

From the above data, the polarisation at infinite dilution ($^{\infty}P_1$ in following table) of each of the solutes was calculated by the expression : $^{\infty}P_1 = A(M_1 - B\beta) + C\alpha$ (for definition of symbols, see Le Fèvre and Russell, this vol., p. 491). The specimen of benzene used in these measurements had $A = 0{\cdot}34085$, $B = 89{\cdot}265$, and $C = 14{\cdot}670$. The figures under ($^{\infty}P_1$) were obtained by graphical estimation. The moments corresponding to these polarisations are shown under μ and (μ) respectively. They have been estimated on the assumption that the $[R_L]_D$ values in the 6th column represent the distortion polarisations.

Substance.	α.	β.	P_1.	($^{\infty}P_1$).	$[R_L]_D$.*	μ.	(μ).
4-Fluorodiphenyl	3·477	0·4277	105·3	98	50	1·50	(1·5)
4-Chlorodiphenyl	3·991	0·5752	105·3	108	55	1·56	(1·6)
4-Bromodiphenyl	4·502	1·053	113·4	117	58	1·64	(1·7)
2-Nitrodiphenyl	20·851	0·6457	354·1	351	56	3·80	(3·8)
4-Nitrodiphenyl	25·107	0·6776	415·5	425	56	4·17	(4·2
4-Aminodiphenyl	5·121	0·4518	119·0	119	55	1·76	(1·8)
4-Acetamidodiphenyl	20·814	0·3494	366·6	360—410	64	3·83	(3·8—4·1)
4-Nitro-4′-aminodiphenyl	58·954	0·4196	925·0	*ca.* 940	62	6·46	(6·5)
4-Bromo-4′-aminodiphenyl	16·351	1·217	287·4	*ca.* 290	63	3·30	(3·3)
4-Bromo-3′-nitro-4′-piperidinodiphenyl	27·945	2·029	471·2	486	89	4·30	(4·4)
Fluorobenzene	2·912	0·1554	70·7	73	26	1·47	(1·5)
Chlorobenzene	3·468	0·2958	80·2	82	31	1·54	(1·6)
Bromobenzene	3·529	0·7188	83·4	84	34	1·55	(1·6)
Nitrobenzene..................................	22·969	0·3891	367·0	*ca.* 360	32	4·03	(4·0)
Aniline	3·509	0·1588	78·4	78	31	1·51	(1·5)
Acetanilide	22·940	0·3487	371·9	370	40	4·01	(4·0)
p-Nitroaniline	56·740	0·5721	862·0	845	37	6·32	(6·3)
p-Bromoaniline	12·158	0·9904	206·8	205	39	2·85	(2·8)
4′-Bromo-2′-nitro-1-phenylpiperidine ...	26·412	1·328	444·2	451	65	4·29	(4·3)

* Calculated on the basis of data given in Landolt–Börnstein–Roth, " Tabellen," 5th Edn., 1923, II, pp. 973—985; Ergänz.-bd. II, 1931, pp. 820—822.

SUMMARY AND CONCLUSION.

The moments of a number of corresponding 1 : 4- and 4 : 4′-substituted benzenes and diphenyls have been measured, and from the mesomerism thereby revealed the inference has been drawn that the independent conjugation of the nuclei in diphenyl derivatives generally is not so complete as might appear from certain earlier discussions on the point.

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